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Identifying the Sources of Nitrate to a Deep Municipal Water Supply Well Using Stable Isotopes of Nitrate, Groundwater Age Dating, and Depth-Specific Sampling

M. J. Singleton¹, R. M. Gailey², J. E. Moran³, M. C. Sutton², N. Heller⁴, B. K. Esser¹, J. R. Philipp²

Attributing the source of nitrate in long-screened production wells is often difficult. This study demonstrates that analysis of natural tracers combined with depth-specific sampling can allow fingerprinting of nitrate source in mixed-age samples drawn from municipal production wells. This study specifically investigates the sources of nitrate contamination to a municipal water supply well in the Central Valley using a combination of natural isotopic and dissolved gas tracers, and an advanced method for profiling chemical concentrations and water flow in long-screened production wells. The municipal well is located near areas of historic and current agricultural activity and screened over four separate vertical depth intervals between 165 and 326 feet below ground surface. Potential sources of nitrate contamination to the well included local almond groves and a fertilizer supply plant located approximately 1000 feet away. Traditional groundwater characterization in this and previous studies sampled private supply wells in the area and monitoring wells on the fertilizer supply plant; data from these studies indicated that the fertilizer supply plant could be a significant source of nitrate to the municipal well. These studies, however, did not address uncertainty in the amount of nitrate contributed by almond groves or in the mechanism for contaminant transport from the fertilizer plant to the municipal well in a region with highly variable groundwater flow direction.

Additional studies included detailed stratigraphic characterization; shallow and deep monitoring well installation, sampling and head monitoring; a pumping test on the municipal well; flow and concentration profiling on the municipal well; groundwater flow and transport modeling (including the well capture zone); and characterization of nitrate stable isotopic composition and ³H-³He groundwater age. The USGS dye tracer and sampling method used at the municipal well allowed depth profiling of flow, nitrate concentration, nitrate isotopic composition, and groundwater age. The isotope and age data provided two new pieces of evidence that the fertilizer supply plant was the source of elevated nitrate in the municipal well.

- 1) Chemical mass balance calculations using nitrate concentration, nitrate isotopic composition, and initial tritium activity all indicated that the source water for elevated nitrate was a very small component of the water produced by the well and thus must have had an extremely high nitrate concentration. The high nitrate concentration (~1500 mg/L as nitrate) required by the mass balance calculations for the source water precluded common agricultural sources of nitrate (such as irrigated agriculture) and was similar to nitrate concentrations in shallow groundwater under the fertilizer plant (>1700 mg/L as nitrate).
- 2) Nitrogen and oxygen isotope compositions of nitrate indicated that the additional anthropogenic nitrate source to the municipal well was significantly enriched in $\delta^{18}\text{O-NO}_3$, an isotopic signature consistent with synthetic nitrate fertilizer, and not with human or animal wastewater discharge, or with organic fertilizer. The fertilizer supply plant handled and stored synthetic nitrate, and monitoring wells on and near the plant had high $\delta^{18}\text{O-NO}_3$.

These findings are consistent with nitrate concentration data indicating that an improperly-constructed industrial water supply well on the fertilizer plant acted as a vertical conduit to deep groundwater at the depth of the municipal well screens.

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Oral Presentation Requested
Forensic Field Characterization and Investigation Techniques

Please note that we have quite a comprehensive analysis to present. While Mike and Rob can share one speaking slot, 1.5 to 2 slots would allow us to convey a much more complete body of information to the conference attendees.

Author Biographies

Michael Singleton is a Staff Scientist in Lawrence Livermore National Laboratory's Chemical Sciences Division where he runs the Stable Isotope Mass Spectrometry Laboratory. Michael's research uses dissolved gas and stable isotope geochemistry to measure groundwater flow and track contaminants through groundwater systems and the vadose zone. Current projects include determining residence times and recharge mechanisms in alpine groundwater systems, and developing new methods using stable isotope forensic signatures to track toxic substances. Michael holds a Ph.D. in Earth and Planetary Sciences from Washington University. Contact information: singleton20@llnl.gov, 925-424-2022, L-231, LLNL, Livermore, CA 94550.

Rob Gailey has been a practicing hydrogeologist since 1985. His work ranges from quantitative analysis to regulatory negotiation and expert witness engagements. Much of it involves water supply wells (i.e., condition assessment, flow and concentration profiling, structural and operations modification for water quality improvement, rehabilitation for performance improvement, and wellfield operations optimization). Rob is a Professional Geologist and Certified Hydrogeologist in California. He earned a B.S. in Geology/Biology from Brown University, an M.S. in Applied Hydrogeology from Stanford University, and an M.B.A. from University of California Berkeley. Contact information: rmgailey@thesourcegroup.net; (415) 407-8407; 3451-C Vincent Road, Pleasant Hill, CA 94523.

Jean Moran is on the faculty in the Department of Earth and Environmental Science at California State University, East Bay. Her research focuses on using natural and artificial isotopes to examine geochemical and transport processes in the vadose zone and in groundwater. Since 2001, she has carried out research on groundwater vulnerability, fate and transport of nitrate, and groundwater transport near artificial recharge areas under the Groundwater Ambient Monitoring and Assessment project sponsored by the California State Water Resources Control Board. Dr. Moran has a Ph.D. in Geochemistry from the University of Rochester, Bachelor's degrees in physics and geology from the University of Rochester and a Master's degree in geophysics from the University of Washington. She has been an author on more than 30 peer-reviewed publications and has been a Groundwater Resources Association of California Board member since January, 2006. Contact information: jean.moran@csueastbay.edu.

Matt Sutton is a Registered Professional Engineer (Civil) in the State of California with over 18 years of project management and engineering experience in the groundwater and environmental consulting and engineering field. He earned a B.S. in Civil Engineering from University of the Pacific. Contact information: msutton@thesourcegroup.net; (925) 944-2856 x 329; 3451-C Vincent Road, Pleasant Hill, CA 94523.

Noah Heller is the President of BESST, Inc. – a company that provides commercial implementation of the United States Geological Survey water supply well profiling and depth-dependent sampling method. A California Professional Geologist with over 25 years experience in the groundwater industry, he has managed over 260 well profiling projects since BESST began using the USGS method in 2005. These projects include wells impacted with nitrates, arsenic, TCE/PCE, manganese, iron, bacteria, fluoride and TDS. Noah holds a B.A in Geology from Rutgers University and an M.S. in Geology from Mississippi State University. Contact information: nheller@besstinc.com; 866-298-8701; 50 Tiburon St., Suite 7, San Rafael, CA 94901.

Brad Esser is a staff scientist at Lawrence Livermore National Laboratory, where he is group leader for Environmental Radiochemistry and the lead for the LLNL Environmental Monitoring Radioanalytical Laboratory. He also leads LLNL's effort in the State of California Groundwater Ambient Monitoring & Assessment (GAMA) program. Brad has a B.S. in Geosciences from the

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University of Arizona and a Ph.D. in Geochemistry from Yale University. His research interests include the use of groundwater age-dating, isotope biogeochemistry, and reactive transport modeling to develop better tools for water resource management, especially with regards to groundwater nitrate. Contact information: bkessler@llnl.gov; 925-422-5247, L-231, LLNL, Livermore, CA 94550.

Jon Philipp is a California Professional Geologist and Certified Hydrogeologist with eleven years of experience on water supply and contaminant projects in California. He has performed well profiling and data analysis for several projects. Jon earned a B.S. in Geology from the State University of New York at Stony Brook and an M.A. in Geology from Johns Hopkins University. Contact information: jphilipp@thesourcegroup.net; (925) 944-2856 x 316; 3451-C Vincent Road, Pleasant Hill, CA 94523.

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